LOCATING CARBON NANOTUBES (CNTS) AT THE SURFACE OF POLYMER MICROSPHERES USING POLY(VINYL ALCOHOL) GRAFTED CNTS AS DISPERSION CO-STABILIZERS

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In this poster, we report first on the grafting of poly(vinyl acetate) (PVAc) on carbon nanotubes by Cobalt Mediated Radical Polymerization (CMRP) using bis(acetylacetonato)cobalt(II) complex ($Co(acac)_2$) as controlling agent. This modification is important to (i) enhance the CNTs affinity for organic media, (ii) promote the solubility of CNTs in water after hydrolysis of the grafted PVAc chains into poly(vinyl alcohol) (PVA), and (iii) impart to CNTs stabilizing properties for dispersion polymerizations of vinyl monomers when partially hydrolyzed PVAc is used. This last point constitutes the second objective of the poster, i.e. demonstrating that CNTs grafted by partially hydrolyzed PVAc are able to stabilize a dispersion polymerization of methyl methacrylate (MMA) with the formation of polymer microspheres containing CNTs mainly located at their surface.

Poly(vinyl acetate) end-capped by $Co(acac)_2$ (PVAc-$Co(acac)_2$) (Mn = 6000 g/mol; Mw/Mn = 1.4) was prepared using 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) as initiator and $Co(acac)_2$ as controlling agent in the bulk at 30°C following a previously reported procedure[1,2]. At the end of the polymerization, the residual monomer was removed under vacuum and degassed methanol was added. This methanolic solution was then added to the CNTs, followed by the addition of a low amount of water at 30°C that activates the C-Co bond homolytic cleavage in mild conditions and consequently releases PVAc° radicals that are rapidly trapped by CNTs following a well-known radical addition to the sp^2 carbons of the CNTs sidewalls. After extensive washing with methanol to remove ungrafted PVAc and released cobalt complex, the modified CNTs contain 20wt% of grafted PVAc (CNTs-g-PVAc), as determined by thermogravimetric analysis (TGA). After partial hydrolysis of PVAc, a dispersion polymerization of MMA in methanol is then carried out in the presence of low amount of modified CNTs (CNTs-g-P(VAc-co-VA)) (1wt% as compared to MMA) and a small amount of conventional free stabilizer (P(VAc-co-VA) (68% hydrolysis); 1.66 wt% as compared to MMA). In the case of pristine CNTs, most of the polymer precipitates as large particles (> 500 µm) although some microspheres are also observed. In contrast, when the same polymerization is carried out in the presence of the modified CNTs (CNTs-g-P(VAc-co-VA)) instead of pristine CNTs, PMMA microspheres smaller than 10 µm are formed without any precipitation. Moreover, CNTs can be observed at the microspheres surface.

References

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2. A. Debuigne, J.-R. Caille and R. Jerome, *Angew. Chem., Int. Ed.*, 2005, **44**, 1101-1104, S1101/1101-S1101/1103.